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Preparation of Tetrakis(arylisocyanide)trialkylphosphitecobalt(I) Complexes with Sterically-hindered Arylisocyanides*

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Abstract

The complexes, $[Co(CNC_6H_3Et_2\text{-}2,6)_4P(OR')_3]X$, $X = BF_4$, ClO_4; $R' = Me$, Et, $CHMe_2$; are prepared by trialkylphosphite substitution reaction in $[Co(CNC_6H_3Et_2\text{-}2,6)_5]X$. The $[Co(CNC_6H_3Me_2\text{-}2,6)_3\{P(OCHMe_2)_3\}_2]ClO_4$ is prepared, and $P(OSiMe_3)_3$ fails to substitute, under analogous reaction conditions. Ease of disubstitution, in preference to monosubstitution, appears to be controlled by steric hindrance of the arylisocyanide, with $2,6\text{-}Et_2C_6H_3NC \ll 2,4,6\text{-}Me_3C_6H_2NC \lesssim 2,6\text{-}Me_2C_6H_3NC \ll o\text{-}MeC_6H_5NC \lesssim C_6H_5NC$; and apparent trialkylphosphite reactivity, $P(OSiMe_3)_3 \ll P(OCHMe_2)_3 < P(OEt)_3 < P(OMe)_3$; but monosubstituted complexes, in general, are conveniently prepared only from $[Co(CNC_6H_3Et_2\text{-}2,6)_5]X$. Melting (decomposition) ranges, ν(-N≡C), and electronic spectra of the new complexes are discussed, herein. Trends seem to parallel those previously observed for triarylphosphine-substituted arylisocyanide–cobalt(I) complexes.

Introduction

Trialkylphosphites have been used extensively as ligands for cobalt(I) complexes. Pentakis(trialkylphosphite)cobalt(I) complexes, $[Co\{P(OR')_3\}_5]X$, $P(OR')_3 = P(OCH_2)_3CCH_3$ [1], $P(OCH)_3(CH_2)_3$ [2, 3], $P(OMe)_3$ [2–5], $P(OEt)_3$ [6, 7] and $[Co\{P(OMe)_3\}_2\{P(OCH_2)_3CEt\}_3]BPh_4$ [4]; have been prepared in a number of different ways. Trialkylphosphites have also been used extensively in ligand substitution and/or addition reactions in cobalt(I) complexes with carbonyls [4, 8–10], organoisocyanides [5, 10–14], hydrides [8, 9, 15], and halides [6, 16].

Reaction of trialkylphosphites with pentakis(arylisocyanide)cobalt(I) producted complexes of the general formula, $[Co(CNR)_3\{P(OR')_3\}_2]X$ ($X = ClO_4$, BF_4), where $R' = Me$, $R = C_6H_5$, $C_6H_4F\text{-}p$, $C_6H_4Cl\text{-}p$, $C_6H_4Br\text{-}p$, $C_6H_4I\text{-}p$, $C_6H_4Me\text{-}p$, $C_6H_3Me_2\text{-}2,6$; and $R = C_6H_4Cl\text{-}p$, $R' = Me$, Et, $CHMe_2$ [12]. Reaction conditions were excess trialkylphosphite (10:1 molar ratio) and limited reaction time (3–5 min). The $[Co(CNR)_3\{P(OMe)_3\}_2]ClO_4$, $R = C_6H_5$, $C_6H_4NO_2\text{-}p$, $C_6H_3Me_2\text{-}2,6$; were also prepared by direct reaction of anhydrous $CoCl_2$, $P(OMe)_3$, and CNR in ethanol in 1:3.5:2.5 molar ratio, respectively [10]. Only $[Co(CNC_6H_4Cl\text{-}p)_3\{P(OMe)_3\}_2]BF_4$ was isolated when $[Co\{P(OMe)_3\}_5]BF_4$ was treated with different mole ratios of $CNC_6H_4Cl\text{-}p$ in CH_2Cl_2 [5]. Thus a 3:2 arylisocyanide:trialkylphosphite ligand ratio in Co(I) complexes was initially well-established.

Preparation of $[Co(CNC_6H_2Me_3\text{-}2,4,6)_3\{P(OMe)_3\}_2]BF_4$ and $[Co(CNC_6H_2Me_3\text{-}2,4,6)_4P(OMe)_3]BF_4$ [14], however, established the possibility of monosubstitution in pentakis(arylisocyanide)cobalt(I) by trialkylphosphites, albeit with sterically hindered arylisocyanides. This present work investigates trialkylphosphite substitution in $[Co(CNC_6H_3Et_2\text{-}2,6)_5]X$ ($X = BF_4$, ClO_4), a cobalt(I) complex observed to monosubstitute exclusively in ligand substitution reaction with triarylphosphines [17, 18] and trialkylphosphines [19].

Experimental

The $[Co(CNR)_5]X$, $X = ClO_4$, $R = 2,6\text{-}Et_2C_6H_3$, $2,6\text{-}Me_2C_6H_3$; $X = BF_4$, $R = 2,6\text{-}Et_2C_6H_3$; were prepared as previously described [20–22]. Trialkylphosphites, $P(OR')_3$, $R' = Me$, Et, $CHMe_2$; were vacuum distilled under vigorous stirring and tris(trimethylsilyl)phosphite, $P(OSiMe_3)_3$ (Alfa), was used without further purification. Anhydrous diethyl ether was filtered through an alumina column immediately before use. IR spectra were recorded on a Perkin-Elmer 1330 Infrared Spectrophotometer in nujol mull and CH_2Cl_2 (~1%) using 0.106 mm pathlength matched NaCl cells. Electronic spectra were measured in CH_2Cl_2 ($\sim 1.5 \times 10^{-5}$ M) using a Perkin-Elmer 552 UV–Vis Spectrophotometer. Elemental analyses were performed commercially.

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Preparation of [Co(CNC$_6$H$_3$Et$_2$-2,6)$_4$P(OCHMe$_2$)$_3$]BF$_4$

A 500 mg sample of [Co(CNC$_6$H$_3$Et$_2$-2,6)$_5$]BF$_4$ was dissolved in 1.0 ml CH$_2$Cl$_2$, filtered through cotton, and treated with 553 mg P(OCHMe$_2$)$_3$ (1:5 molar ratio) dropwise. After 5 min reaction time at 25 °C, the solution was treated with 13.7 ml ether dropwise to effect precipitation, cooled in ice for 20 min, and filtered. Addition of 4.6 ml ether to the filtrate and extensive cooling (~24 h) effected a second crop of yellow microcrystals. Crude product, 415 mg (79% yield), was recrystallized from 1.0 ml CH$_2$Cl$_2$ and 12.0 ml ether; yield: 300 mg (57%). *Anal.* Calc. for CoC$_{53}$H$_{73}$BF$_4$N$_4$O$_3$P: C, 64.24; H, 7.43; N, 5.65; P, 3.13. Found: C, 64.36; H, 7.37; N, 5.68; P, 3.34%.

Preparation of [Co(CNC$_6$H$_3$Me$_2$-2,6)$_3${P(OCHMe$_2$)$_3$}$_2$]ClO$_4$

A 325 mg sample of [Co(CNC$_6$H$_3$Me$_2$-2,6)$_5$]ClO$_4$ was dissolved in 1.0 ml CH$_2$Cl$_2$ and filtered through cotton. Then 415 mg P(OCHMe$_2$)$_3$ (1:5 molar ratio) was added dropwise with swirling. After 5 min reaction time at 25 °C, 5.0 ml ether was added dropwise to effect precipitation. After thorough cooling in ice for 30 min, the pale yellow microcrystals were collected on a sintered-glass frit and dried under suction/air. Addition of excess ether to the filtrate and prolonged refrigeration (2–3 days) produced an insignificant amount of second crop. Crude product was recrystallized from 1.0 ml CH$_2$Cl$_2$ and 4.0 ml ether; yield: 210 mg (54%). *Anal.* Calc. for CoC$_{45}$H$_{69}$ClN$_3$O$_{10}$P$_2$: C, 55.81; H, 7.18; N, 4.34; P, 6.40. Found: C, 55.92; H, 7.01; N, 4.44; P, 6.40%.

Preparation of [Co(CNC$_6$H$_3$Et$_2$-2,6)$_4$P(OEt)$_3$]ClO$_4$

A 500 mg sample of [Co(CNC$_6$H$_3$Et$_2$-2,6)$_5$]ClO$_4$ was dissolved in 1.0 ml CH$_2$Cl$_2$ and filtered through cotton. Then 435 mg P(OEt)$_3$ (1:5 molar ratio) was rapidly added, dropwise. Golden yellow crystals were isolated after 5 min reaction time by dropwise addition of 17.0 ml ether to effect precipitation. Crude product was cooled in ice for 45 min, filtered, and dried under suction/air; 389 mg (77% yield). The pure compound was obtained by recrystallization first from 1.0 ml CH$_2$Cl$_2$ and 15.0 ml ether (305 mg, 61%); then from 1.0 ml CHCl$_3$ and 10.0 ml ether; final yield: 257 mg (51%). *Anal.* Calc. for CoC$_{50}$H$_{67}$ClN$_4$O$_7$P: C, 62.46; H, 7.02; N, 5.83. Found: C, 62.72; H, 7.26; N, 5.46%.

Preparation of [Co(CNC$_6$H$_3$Et$_2$-2,6)$_4$P(OMe)$_3$]BF$_4$

A 500 mg sample of [Co(CNC$_6$H$_3$Et$_2$-2,6)$_5$]BF$_4$ was dissolved in 1.0 ml CH$_2$Cl$_2$, filtered through cotton, and treated with 330 mg P(OMe)$_3$ (1:5 molar ratio). After 10 min reaction time at room temperature, a dropwise addition of 9.5 ml ether and prolonged cooling in ice for ~5.5 h produced a small amount (~10 mg) of sticky yellow-orange solid. Addition of 1.5 ml ether to this filtrate and extensive refrigeration for ~4 days produced a second crop of yellow crystals (80.5 mg). Crude product was recrystallized from CH$_2$Cl$_2$/ether; yield: 58 mg (12%). *Anal.* Calc. for CoC$_{47}$H$_{61}$BF$_4$N$_4$O$_3$P: C, 62.26; H, 6.78; N, 6.18; P, 3.42. Found: C, 61.95; H, 6.68; N, 6.14; P, 3.61%.

Results and Discussion

Preparation of Complexes/Substitution Preference

Preparation of [Co(CNC$_6$H$_3$Et$_2$-2,6)$_4$P(OCHMe$_2$)$_3$]BF$_4$ and [Co(CNC$_6$H$_3$Me$_2$-2,6)$_3${P(OCHMe$_2$)$_3$}$_2$]ClO$_4$ were straightforward and in good yields, underscoring the marked preference for monosubstitution in [Co(CNC$_6$H$_3$Et$_2$-2,6)$_5$]X over [Co(CNC$_6$H$_3$Me$_2$-2,6)$_5$]X. Since [Co(CNC$_6$H$_3$Me$_2$-2,6)$_3${P(OMe)$_3$}$_2$]ClO$_4$ was previously prepared [12], the [Co(CNC$_6$H$_3$Me$_2$-2,6)$_5$]X apparently has a tendency to disubstitute with trialkylphosphites as well as triarylphosphines [17]. Since [Co(CNC$_6$H$_2$Me$_3$-2,4,6)$_4$P(OMe)$_3$]BF$_4$ was isolated with some difficulty [14], however, trialkylphosphite substitution most probably parallels triarylphosphine substitution in that ease of disubstitution and difficulty of preparing pure monosubstituted complex is controlled by steric hindrance of the arylisocyanide: 2,6-Et$_2$C$_6$H$_3$NC $\ll$ 2,4,6-Me$_3$C$_6$H$_2$NC $\lesssim$ 2,6-Me$_2$C$_6$H$_3$NC $\ll$ *o*-MeC$_6$H$_4$NC $\lesssim$ C$_6$H$_5$NC [17]. Thus, [Co(CNC$_6$H$_3$Me$_2$-2,6)$_4$P(OR')$_3$]X should be preparable with sufficient patience; that solubilities, in general, follow [Co(CNR)$_3${P(OR')$_3$}$_2$]X < [Co(CNR)$_4$P(OR')$_3$]X < [Co(CNR)$_5$]X making purification of the monosubstituted derivative in a mixture rather difficult.

Both P(OMe)$_3$ and P(OEt)$_3$ showed some tendency for disubstitution, as well as monosubstitution, with [Co(CNC$_6$H$_3$Et$_2$-2,6)$_5$]X. The [Co(CNC$_6$H$_3$Et$_2$-2,6)$_4$P(OEt)$_3$]ClO$_4$ was purified by double recrystallization, but preparation of pure [Co(CNC$_6$H$_3$Et$_2$-2,6)$_4$P(OMe)$_3$]BF$_4$ was tedious and in poor yield due to a tendency to oil in the presence of excess P(OMe)$_3$. Mixtures of [Co(CNC$_6$H$_3$Et$_2$-2,6)$_4$P(OMe)$_3$]BF$_4$ and [Co(CNC$_6$H$_3$Et$_2$-2,6)$_3${P(OMe)$_3$}$_2$]BF$_4$, surprisingly, could be initially crystallized more easily. Attempted preparation of pure [Co(CNC$_6$H$_3$Et$_2$-2,6)$_3${P(OMe)$_3$}$_2$]BF$_4$ with 10:1 mole ratio P(OMe)$_3$ and 10 min reaction time was unsuccessful; elemental analysis of the product after one CH$_2$Cl$_2$/ether recrystallization indicated 65–60% [Co(CNC$_6$H$_3$Et$_2$-2,6)$_4$P(OMe)$_3$]BF$_4$ and 35–40% [Co(CNC$_6$H$_3$Et$_2$-2,6)$_3${P(OMe)$_3$}$_2$]BF$_4$. Again, with sufficient patience, a pure compound could probably be obtained.

Reaction of P(OSiMe$_3$)$_3$ in 5:1 and 10:1 mole ratio with [Co(CNC$_6$H$_3$Et$_2$-2,6)$_5$]BF$_4$ for 10 min and 30 min reaction periods, respectively, was also unsuccessful in that principally unsubstituted $[Co(CNR)_5]BF_4$ was recovered (~65%), although a second crop suggested the presence of a small amount of new complex. Reactivity of the trialkylphosphites, therefore, seems to follow $P(OSiMe_3)_3 \ll P(OCHMe)_2)_3 < P(OEt)_3 < P(OMe)_3$. Decreased reactivity could be due to increased electron donation of the substituents leading to decreased π^*-acceptance and an increased σ-donation by the P coordination site and/or increased steric hindrance in the trialkylphosphite. Triarylphosphine monosubstitution and disubstitution reactions are sensitive to electron-induction effects from the phosphine substituents [18], but $P(NEt_2)_3$ monosubstitution reactions appear to be sterically controlled [19]. More investigation is necessary to draw firm conclusions.

Trialkylphosphite monosubstitution is not entirely restricted to sterically-hindered arylisocyanides, however, as indicated by IR data on unrecrystallized samples. In both reactions of $[Co(CNC_6H_4Cl\text{-}p)_5]BF_4$ with 1:1.1 mole ratio $P(OMe)_3$ for 1 h in CH_2Cl_2 and $[Co\{P(OMe)_3\}_5]BF_4$ with 1:10 mole ratio $CNC_6H_4Cl\text{-}p$ for 20 min, the crude product exhibited a weak band at 2185 cm^{-1} (nujol), as well as stronger bands appropriate to $[Co(CNC_6H_4Cl\text{-}p)_3\{P(OMe)_3\}_2]BF_4$. This band is certainly the medium intensity, highest energy ν(-N≡C) in the monosubstituted complex. The small amount of $[Co(CNC_6H_4Cl\text{-}p)_4P(OMe)_3]BF_4$, and monosubstituted derivatives probably formed in other trialkylphosphite reactions, was removed and/or lost in routine recrystallization, and was, thus, initially undetected [11, 12]. Considering the difficulty or near impossibility of isolating pure samples of triphenylphosphine-monosubstituted Co(I) complexes with non-sterically hindered arylisocyanides: $[Co(CNR)_4P(C_6H_5)_3]ClO_4$, R = $C_6H_4Cl\text{-}p$, $C_6H_4Br\text{-}p$ [17]; $C_6H_4Me\text{-}p$ [23] (however, see comments in refs. [17, 24]) and the relative ease of preparing pure $[Co(CNR)_4P(C_6H_5)_3]ClO_4$ with R = 2,6-$Me_2C_6H_3$ and 2,4,6-$Me_3C_6H_2$ as well as 2,6-$Et_2C_6H_3$ [17], one can speculate that monosubstituted trialkylphosphite complexes could be reasonably prepared only with sterically hindered arylisocyanides.

Physical Properties of the new Complexes

Physical properties of melting (decomposition) range, CH_2Cl_2 and nujol ν(-N≡C) frequencies, and electronic spectra λ_{max} and ϵ (molar extinction) values for the new Co(I) complexes and the $[Co(CNR)_5]X$ parent complex are listed in Table I. The new compounds are yellow microcrystals, the disubstituted being lighter (pale yellow) than the monosubstituted (medium to golden yellow), a color trend analogous to triarylphosphite [25] and trialkylphosphine [19] complexes but reversed from triarylphosphine [17]. Melting (decomposition) ranges for the $[Co(CNC_6H_3Et_2\text{-}2,6)_4P(OR')_3]X$ vary R' = $CHMe_2$ > Et > Me, the reverse of the trend for $[Co(CNC_6H_4Cl\text{-}p)_3\{P(OR')_3\}_2]X$ [12], but parallel in ease of preparation. The disubstituted $[Co(CNC_6H_3Me_2\text{-}2,6)_3\{P(OCHMe_2)_3\}_2]ClO_4$ has a higher decomposition range than monosubstituted $[Co(CNC_6H_3Et_2\text{-}2,6)_4P(OCHMe_2)_3]BF_4$, analogously with triarylphosphine [17, 18, 26] and trialkylphosphine [19] complexes. The thermally most stable monosubstituted complex, $[Co(CNC_6H_3Et_2\text{-}2,6)_4P(OCHMe_2)_3]BF_4$, has a decomposition range below its analogous $P(C_6H_5)_3$ complex [17] but above the analogous $P(C_6H_4Cl\text{-}p)_3$, $P(C_6H_4OMe\text{-}p)_3$ [18] and $P(C_2H_4CN)_3$, $P(C_6H_{13}\text{-}n)_3$, $P(NEt_2)_3$ [19] complexes. Decomposition ranges thus reflect ease of preparation and apparent stability.

Representative IR spectra for these complexes are pictured in Fig. 1. The $[Co(CNC_6H_3Et_2\text{-}2,6)_4P(OCHMe_2)_3]BF_4$, Fig. 1B, has the four-band pattern characteristic of monosubstituted triarylphosphine and trialkylphosphine complexes [17, 19] but not triarylphosphite [25]. The $[Co(CNC_6H_3Me_2\text{-}2,6)_3\{P(OCHMe_2)_3\}_2]ClO_4$ (Fig. 1C) has a doubled

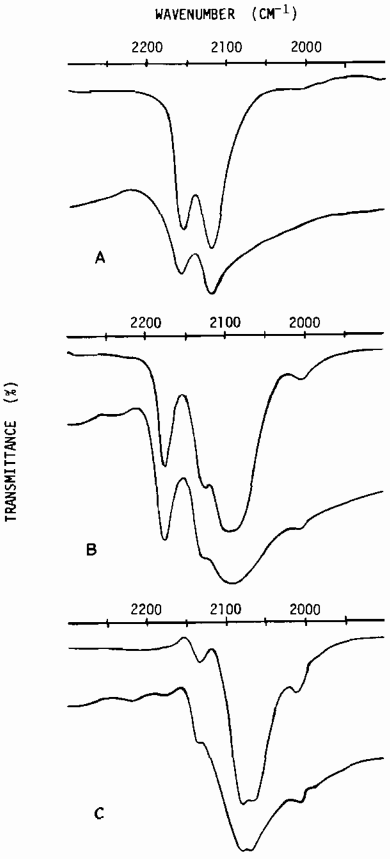

Fig. 1. Selected IR spectra (2300–1950 cm^{-1}; top, CH_2Cl_2; bottom, nujol) for cobalt(I) complexes; (a) $[Co(CNC_6H_3Et_2\text{-}2,6)_5]BF_4$; (B) $[Co(CNC_6H_3Et_2\text{-}2,6)_4P(OCHMe_2)_3]BF_4$; (C) $[Co(CNC_6H_3Me_2\text{-}2,6)_3\{P(OCHMe_2)_3\}_2]ClO_4$.

TABLE I. Physical Properties of Selected Arylisocyanide–Cobalt(I) Complexes

Compound	Melting point[a] (°C)	Isocyanide IR[b]		Electronic spectra[c]
		$\mathrm{CH_2Cl_2}$	Nujol	
$[\mathrm{Co(CNC_6H_3Et_2\text{-}2,6)_5]BF_4}$	208–211	2119vs 2156s	2119vs 2159s	322(24000) ~288sh 259(65000) ~234sh 224(47000)
$[\mathrm{Co(CNC_6H_3Me_2\text{-}2,6)_5]ClO_4}$	87–105	2120vs 2154s	2112vs(br) 2152s(br)	322(12000) ~291sh 254(32000) ~237sh 232(42000)
$[\mathrm{Co(CNC_6H_3Me_2\text{-}2,6)_3\{P(OCHMe_2)_3\}_2]ClO_4}$	183–187	2011w 2065s 2078s 2133w	2007vw(sh) 2067s 2078s 2133w	325(6800) 263(81000) ~240sh 218(37000)
$[\mathrm{Co(CNC_6H_3Et_2\text{-}2,6)_4P(OCHMe_2)_3]BF_4}$	159–161	~2006vw(sh) 2096vs(br) 2126w 2177m	~2006vw(sh) 2094vs(br) ~2126w(sh) 2177m	318(20000) ~290sh 261(66000) ~238sh 224(46000)
$[\mathrm{Co(CNC_6H_3Et_2\text{-}2,6)_4P(OEt)_3]ClO_4}$	144–150	~2008vw(sh) 2087vs 2128w 2177m	~2006vw(sh) 2084vs(br) ~2131w(sh) 2179m	321(19000) ~290sh 260(52000) ~240sh ~233sh 225(41000)
$[\mathrm{Co(CNC_6H_3Et_2\text{-}2,6)_4P(OMe)_3]BF_4}$	112–115	~2008vw 2098vs(br) ~2110w(sh) ~2126vw(sh) 2177m	~2014vw(sh) ~2096vs(br) ~2135w(sh) 2180m	324(25000) ~289sh 258(58000) ~235sh 224(44000)

[a] Melting (decomposition) range, uncorrected. [b] The ν(-N≡C) in $\mathrm{cm^{-1}}$; s = strong, m = medium, w = weak, v = very, sh = shoulder, br = broad. [c] The $\lambda_{max}(\epsilon)$ in mμ (nm) without Gaussian resolution.

dominant band, atypical of most disubstituted arylisocyanidecobalt(I) complexes but characteristic with o-$\mathrm{MeC_6H_4NC}$ and 2,6-$\mathrm{Me_2C_6H_3NC}$ [17–19]. The dominant ν(-N≡C) for $[\mathrm{Co(CNC_6H_3Me_2\text{-}2,6)_3\{P(OCHMe_2)_3\}_2]ClO_4}$ is significantly lower than for $[\mathrm{Co(CNC_6H_3Et_2\text{-}2,6)_4P(OCHMe_2)_3]BF_4}$, as anticipated when two, instead of one, trialkylphosphite ligands replace the stronger π^*-accepting and weaker σ-donating RNC. The ν(-N≡C) values for $[\mathrm{Co(CNC_6H_3Et_2\text{-}2,6)_4P(OR')_3]X}$ would be expected to follow R′ = $\mathrm{CHMe_2}$ < Et < Me, as in $[\mathrm{Co(CNC_6H_4Cl\text{-}}p)_3\mathrm{\{P(OR')_3\}_2]X}$ [12] but this trend is not observed. The dominant band is very broad, even in solution, making precise estimation of ν(-N≡C) difficult, but steric hindrance could be causing deviation from expected behavior. Infrared values for the sterically-hindered $[\mathrm{Co(CNCMe_3)_3\{P(NMe_2)_3\}_2]ClO_4}$ were also anomalous [27].

Representative electronic spectra for these complexes are shown in Fig. 2. An analogous pattern is observed from $[\mathrm{Co(CNR)_5]X}$ to $[\mathrm{Co(CNR)_4L]X}$ to $[\mathrm{Co(CNR)_3L_2]X}$ [12, 18, 19, 26–29]. The ϵ values are significantly lower than for analogous triarylphosphine complexes [18] but comparable to trialkylphosphine complexes [19], the expected behavior for aliphatic ligands *vs.* aromatic. The ϵ values are still large enough for interpretation as all metal-to-ligand charge-transfer bands [12, 26, 30], rather than as one crystal field band and the rest charge-transfer bands [29, 31]. Wavelength for the first electronic transition in $[\mathrm{Co(CNC_6H_3Et_2\text{-}2,6)_4P(OR')_3]X}$ follows R′ = $\mathrm{CHMe_2}$ < Et < Me, contrary

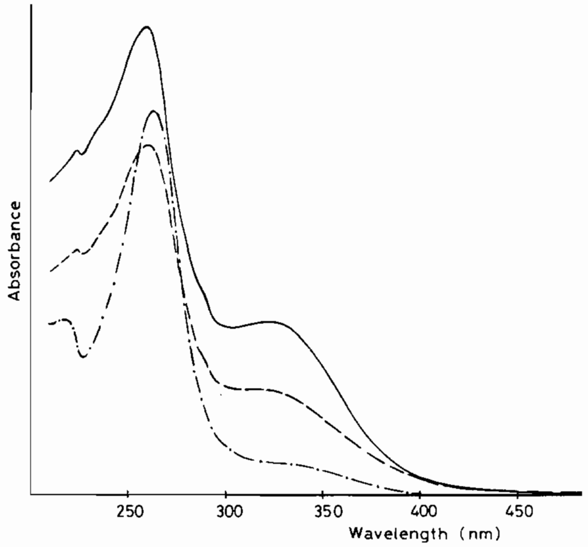

Fig. 2. Solution electronic spectra (CH_2Cl_2, 25 °C) for selected cobalt(I) complexes; $[Co(CNC_6H_3Et_2\text{-}2,6)_5]BF_4$ (——); $[Co(CNC_6H_3Et_2\text{-}2,6)_4P(OCHMe_2)_3]BF_4$ (- - -); and $[Co(CNC_6H_3Me_2\text{-}2,6)_3\{P(OCHMe_2)_3\}_2]ClO_4$ (- · -).

to expected behavior for a $d_\pi \rightarrow \pi^*$ (equatorial) transition [12, 18, 19, 26, 27] and an increasing σ-donating/decreasing π*-accepting ability; $P(OMe)_3 < P(OEt)_3 < P(OCHMe_2)_3$. The λ_{max} displacements for triarylphosphine-monosubstituted complexes are smaller than for analogous disubstituted [18] but a trend in these trialkylphosphite derivatives should still be observable. Considering the steric hindrance in these complexes and the lack of C_{3v} symmetry for solution structures with less sterically-hindered ligands [32], however, interpretation of these electronic spectra may not be feasible. Steric hindrance could be overriding inductive effects in both infrared and electronic data.

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